Study of the reactivity of organonickel sigma-complexes towards nitriles

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The reactivity of organonickel sigma-complexes of type [NiBr(Ar)(bpy)], where Ar = 2,6-dimethylphenyl (Xyl), 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl (Tipp), 2,4,6-tricyclohexylphenyl (Tchp), bpy = 2,2′-bipyridine, towards nitriles (acetonitrile, propionitrile, chloroacetonitrile, benzonitrile) has been investigated. This reaction leads to imines by formation of new carbon—carbon bond between aromatic fragment and nitrile group C≡N.

Key words: 2,2′-bipyridine, imines, organonickel sigma-complexes, nitriles, mass spectrometry, X-ray analysis, electrosynthesis.

The use of transition metal complexes in catalytic conversion of organic compounds is one of the most promising directions of development in modern chemistry.[1] Organometallic sigma-complexes are main intermediates of catalytic processes involving organic substrates. Application of nickel complexes as catalysts for coupling reactions, leading to the formation of organic and organophosphorus compounds, is actual and of practical demand due to availability and relatively low cost of nickel derivatives.[2] Particular attention has recently been given to processes based on the use of highly reactive organometallic intermediates, representing the products of the reaction of organic substrate with an active form of the metal complex catalyst.[3] Such active particles in the processes of homo- and cross-coupling involving organic halides are organonickel sigma-complexes, which could be stabilized and isolated in pure form by using *ortho*-substituted aromatic halides.[4] The substituents in the *ortho*-positions of aromatic ring, sigma-bonded with nickel atom, restrict free rotation around sigma metal-carbon bond and shield the axial positions of metal center.[5] However, at present almost no data on the reactivity of organonickel sigma-complexes towards unsaturated compounds, in particular, to nitriles, are available. At the same time, the processes of activation and functionalization of organic derivatives containing carbon-nitrogen multiple bonds in the coordination sphere of the transition metal complexes have been studied in some detail.[6—12]

The aim of this work is to investigate the reactivity of organonickel sigma-complexes of the type [NiBr(Ar)(bpy)] (Ar is 2,6-di- or 2,4,6-tri-substsituted phenyl, bpy is 2,2′-bipyridine) towards nitriles.

Results and Discussion

The series of organonickel sigma-complexes **1—4** of the composition [NiBr(Ar)(bpy)] (Ar is 2,6-dimethylphenyl (Xyl), 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl (Tipp), 2,4,6-tricyclohexylphenyl (Tchp)) were prepared according to earlier developed procedure,[13—15] which includes oxidative addition of electrochemically generated [Ni^0(bpy)] complexes to corresponding aromatic bromides (Scheme 1).

First, it has been experimentally established that by dissolving of sigma-complex **2** in acetonitrile in the absence of intentionally added reagents, capable to decoordinate bromide anion from the coordination sphere of nickel, the reaction of complex **2** with the solvent (MeCN) molecules proceeds sufficiently slow (8 h). That can be judged by the change of the solution color from intensive red to greenish-yellow. This color change is associated with a cleavage of aryl moiety sigma-bonded to the nickel atom. The aryl moiety is a ligand of strong field, and it ensures the realization of low-spin state (16e-complex, dsp^2-hybridization) of the metal center.[2] This is followed by the formation of new carbon-carbon bond between the aryl moiety and carbon atom of the nitrile group C≡N.

It was established previously[16] that DMF molecules are capable to substitute the bromide anion in the coor-

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